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Stability of Bromine, Iodine Monochloride, Copper (II) Chloride, and Nickel (II) Chloride Intercalated Pitch-Based Graphite Fibers

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(NASA-TM-89904) STABILITY OF BROMINE, ICDIDE MONOCHIORIIE, CCPPER (II) CHLORIDE, AND NICKEL (II) CHLORIDE INTERCALATED PITCH-BASED GRAPHITE FIBERS (NASA) 18 P CSCL 11G G3/27 Unclas 0079712
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STABILITY OF BROMINE, IODINE MONOCHLORIDE, COPPER (II) CHLORIDE, AND NICKEL (II) CHLORIDE INTERCALATED PITCH-BASED GRAPHITE FIBERS

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SUMMARY

Four different grades of pitch-based graphite fibers (Amoco P-55, P-75, P-100, and P-120) were intercalated with each of four different intercalates: bromine (Br_2), iodine monochloride (ICl), copper (II) chloride ($CuCl_2$), and nickel (II) chloride ($NiCl_2$). The P-55 fibers did not react with Br_2 or $NiCl_2$, and the P-75 did not react with $NiCl_2$. The stability of the electrical resistance of the intercalated fibers was monitored over long periods of time in ambient, high humidity (100 percent at 60 °C), vacuum (10^{-6} torr), and high temperature (up to 400 °C) conditions. It was found that fibers with lower graphitization form graphite intercalation compounds (GIC's) which are more stable than those with higher graphitization (i.e., P-55 (most stable) > P-75 > P-100 > P-120 (least stable)). Br_2 formed the most stable GIC's followed in order of decreasing stability by ICl, $CuCl_2$, and $NiCl_2$. While Br_2 GIC's had the best stability, ICl had the advantages of forming GIC's with slightly greater reduction in resistance (by about 10 percent) than Br_2, and the ability to intercalate P-55 fiber. The transition metal chlorides appear to be seriously susceptible to water vapor and high temperature. However, it should be cautioned that matrix effects when these fibers are made into composites may cause the composite stabilities to differ from these single fiber results.

E-3431

INTRODUCTION

Carbon and graphite fibers are being utilized in increasing quantities in the aerospace industry because of their high strength (up to 3.4 GPa), high modulus (up to 830 GPa), and low density (1.76 to 2.18 gm/cm^3). But there are also a large number of potential applications that arise because of the low electrical resistivity of these fibers (resistivities as low as 220 μΩ-cm). The number of applications increases if the resistivity of the fibers can be lowered even further (ref. 1).

There are three forms of graphite fiber available at this time. By far the most widely used fibers are formed from the pyrolosis of polyacrylonitrile

(PAN) fibers. They have the broadest application because of their high strength and low cost. Fibers spun from mesophase pitch have been developed for stiffness critical applications. They have very high elastic modulus, but their strength is lower than the PAN fibers, and their cost is much higher. The third type of fiber is grown from the chemical vapor deposition and subsequent pyrolysis of hydrocarbon-hydrogen mixtures. These fibers have very high electrical and thermal conductivity, but are still only experimentally produced.

The resistivities of pitch-based and vapor-grown graphite fibers can be lowered by intercalation, that is, by inserting guest atoms or molecules between the graphene planes. The guests can act either as electron donors or acceptors, which increases the number of charge carriers in the graphite. Resistivities lower than that of silver have been reported for some GIC's (ref. 2). Unfortunately, to date there has been little success intercalating PAN-based graphite fibers (ref. 3).

One fundamental problem that has hindered the commercial application of intercalated graphite fibers is their reactivity with atmospheric oxygen and water. Recently, residual Br_2 GIC's have emerged as possessing much better stability characteristics in pitch-based P-100 fibers than transition metal chlorides, long considered the most stable intercalates (ref. 4). But P-100 fibers are expensive and do not offer suitable mechanical characteristics for many applications. Subsequent study with the residual Br_2 GIC's of a variety of pitch-based fibers revealed that similar gains in conductivity were achieved with all of the fibers which were graphitic enough to intercalate. Additionally, the thermal stability was increased with decreasing graphitization of the fibers (ref. 5). The purpose of this study is to determine if these are generalized phenomena, or peculiar to the Br_2-graphite fiber system.

METHODS AND MATERIALS

Fibers used in this study were pitch based P-120, P-100, P-75, and P-55 manufactured by Amoco (formerly by Union Carbide). They were intercalated by standard techniques which have been detailed elsewhere (refs. 4, 6, and 7).

Fibers were mounted on four point resistance measuring plates using carbon paint (Structure Probe Inc.) (ref. 1). Plates used for the temperature tests above 150 °C were made of platinum leads sputtered on aluminum oxide substrates. Plates used for all other tests were made from copper leads on integrated circuit boards. A 100 μA current was supplied to the outer contacts using a Keithley 225 constant current source, and the potential drop was measured across the inner contacts using a Keithley 181 nanovoltmeter. Measurements were made at both polarities and averaged to cancel out possible electrochemical effects.

The resistances of the fibers were monitored before the stability tests were begun to ensure that the initial state was a stable residue compound. In the cases of $NiCl_2$ and $CuCl_2$ equilibrium could not be established in the ambient air, so the fibers were brought to equilibrium in a calcium sulfate desiccator.

The vacuum tests were performed by storing the fiber samples in a bell jar in a vacuum of about 10^{-4} Pa (10^{-6} torr). They were removed at intervals for

resistance measurements, but efforts were made to minimize the time they were exposed to ambient laboratory pressure air.

Fibers in the humidity tests were stored in sealed beakers over a water reservoir, and placed in a 60 °C incubator. Fibers of each type were stored in separate beakers to prevent cross contamination. Fibers were removed from the humidity chamber and allowed to cool to room temperature before the fiber resistance was measured. Efforts were made to minimize the time the samples were in the ambient air.

Fibers in the high temperature tests were placed in large thermal mass ovens set to the test temperature. The test temperatures ranged from 100 to 400 °C in increments of 50 °C. The test plates were removed at intervals and placed on an aluminum block to cool them rapidly to room temperature. The resistance measurements were made at room temperature. The large thermal mass of the ovens and the aluminum cooling block minimized the time that the fibers spent at intermediate temperatures.

RESULTS AND DISCUSSION

Intercalation Reactions

The extent of reaction for the fibers was determined by changes in their resistance. The diameters of the fibers were not measured, so the true resistivities are not known, but it is believed that the resistivity calculated using the manufacturer's specified fiber diameter provides an indication of the trends.

Br_2 did not react to an appreciable extent with P-55 fibers, and $NiCl_2$ had little reaction with P-75. $NiCl_2$ intercalation of P-55 was not attempted because of the lack of P-75 reaction. The intercalated fiber resistivities ranged from 44 to 330 μΩ-cm in those intercalation reactions which were considered successful. The results are summarized in table I. ICl consistently gave the largest resistivity decrease, roughly a factor of 5 for P-120, P-100, and P-75, and a factor of 3 for P-55. Br_2 gave comparable results for P-120, P-100, and P-75 fibers, but showed little resistivity change with P-55. The resistivities of $CuCl_2$ and $NiCl_2$ intercalated fibers were slightly higher, but as will be shown later, the instability of the product casts doubt on the initial resistivities of $CuCl_2$ and $NiCl_2$. It seems reasonable to conclude that P-75, P-100, and P-120 all exhibit comparable improvement in resistivity upon intercalation (about a factor of 5), whereas P-55 gives an approximate three-fold increase. The P-55 fiber thus appears qualitatively different from the other three in its ability to be intercalated. It is interesting that these intercalates gave similar factors of improvement, but this is probably not significant in light of the 12-fold resistivity improvement of stage 3 $CuCl_2$ intercalated P-100 (ref. 4).

Ambient Stability

There were qualitative differences between the behavior of the fibers intercalated with the halogens and those intercalated with the transition metal chlorides. While the resistances of the fibers intercalated with the halogens leveled off within a few days of their formation, those of the transition metal

chloride intercalated fibers continued to climb for at least several weeks. It is known that immediately after pitch-based graphite fibers are removed from a Br_2 atmosphere, Br_2 outgasses from the surface of the fiber. In pitch-based fibers this process is essentially complete within a few minutes, though there are small changes for several days (ref. 8). Fibers intercalated with ICl seem to undergo a similar reaction, though on a somewhat longer timescale. In contrast, when $CuCl_2$ and $NiCl_2$ are used as intercalates, they pick up water from the air, as do other transition metal chlorides (ref. 4). The water acts as an electron donor to either the intercalate or possibly to the graphite lattice itself, reducing the number of hole carriers, and thus, raising the resistivity of the fiber. This process is reversible by placing the intercalated and hydrated fibers in a desiccator, or by heating them (ref. 4).

Figure 1 summarizes the resistance changes of the fibers exposed to ambient conditions over a period of several weeks for each of the fiber types and each of the intercalates. None of the fibers which were brominated had any change in resistance over months of exposure to the atmosphere. In fact, Br_2 P-100 fibers have shown no change over a period exceeding 3 years.

P-55 and P-75 fibers intercalated with ICl also showed no resistance increase after several weeks. However, P-100 and P-120 fibers intercalated with ICl showed slight resistance increases (about 1 percent) after several months. While this approaches the error in the measurement, the absolute stability in the resistance measurements for the Br_2 samples and the ICl intercalated P-55 and P-75 lends credence to the reality of some small resistance changes. It is not known whether this is due to slow deintercalation of the fiber, or a slight susceptibility to water or oxygen in the air.

The P-100 and P-120 fibers intercalated with $NiCl_2$ showed considerably larger resistance increases when stored in ambient air. While the increases were well above the error in the measurement, after several weeks they were still less than 5 percent. It should be noted however that these tests were run during the winter when the ambient humidity is low.

P-55 and P-75 fibers intercalated with $CuCl_2$ showed an increase in resistance on ambient air exposure, but only by a few percent. There were large increases in the resistances of P-100 and P-120 fibers intercalated with $CuCl_2$. The large variation in the $CuCl_2$ resistance within each fiber type, compared with the fibers intercalated with ICl and Br_2, probably indicates that the $CuCl_2$ intercalation was incomplete in at least some of the fibers.

It is interesting to note that stage 2 $CuCl_2$ appears to be much less stable than stage 3 $CuCl_2$ in P-100 fibers which were subjected to the same tests (ref. 4). It should be noted, however, that the stage 3 fibers were prepared at NASA Lewis Research Center and the stage 2 fibers were prepared at Intercal Co., so details of the synthesis procedures may differ.

Humidity Stability

If the resistance changes observed in the ambient test can be attributed to the fibers absorbing water from the air, then the humidity test should amplify the results of the ambient air tests. The same general trends which were observed in the ambient tests can be discerned from the plot of resistance ratio (resistance/initial resistance) as a function of time exposed to the high

humidity environment, figure 2. Again, the resistivity of the brominated fibers was unchanged for months-long time periods in the high humidity environment. Also, fibers intercalated with ICl were nearly as stable with resistivity increases of only a few percent after several weeks. In a previous study with ICl intercalated P-100 fibers it was shown that much of the increase in the resistance in these conditions is due to the 60 °C temperatures, rather than the humidity itself (ref. 9).

The resistances of P-100 and P-120 fibers intercalated with $NiCl_2$ more than doubled after 30 min in the high humidity environment. It appears that, in contrast to the results obtained in ambient conditions, the P-100 fiber resistance increased at at faster rate than the P-120. The large sample to sample variations and the uncertainty in the initial resistances may well be responsible for this apparent exception to the rule of "increasing graphitization, decreasing stability." While there was an attempt made to have the fibers initially fully dehydrated, even in the desiccator there was some small increase of resistance with time. Hence, the absolute resistivity values reported in table I may be high, and the resistance ratios reported in figure 2 may be low. This is also true of the $CuCl_2$ intercalated samples.

The clearest trend of the effect of graphitization on humidity stability is evidenced by the results with $CuCl_2$. This is the only intercalate which is substantially effected by humidity and for which samples of all four fiber types were available. P-100 and P-120 intercalated fibers were much less stable than P-75 and P-55 intercalated fibers. Increasing fiber graphitization decreases humidity stability, that is, P-55 (most stable) > P-75 > P-100 > P-120 (least stable). This may well be related to the increased diffusion time of the water through a less perfect lattice. A comparison of the stage 2 $CuCl_2$ intercalated P-100 fiber with its stage 3 counterpart reveals that the deterioration rate is slower in the stage 3 compound, but the final resistance ratios are similar (about 3 in both cases) (ref. 4).

Vacuum Stability

The resistance of each of the fiber types (P-120, P-100, P-75, and P-55) intercalated by each of the intercalates (Br_2, ICl, $CuCl_2$, and $NiCl_2$) were invariant with time exposed to a 10^{-6} torr vacuum for at least several weeks. This implies a strong interaction of the intercalate molecules with the graphite lattice. If there are neutral spacers of the type previously reported (ref. 10), they play no role in either conduction or stabilization of the intercalation compounds.

High Temperature Stability

The effects of fiber graphitization on the high temperature stability of brominated P-75, P-100, and P-120 fibers is shown in figure 3. As was reported earlier (ref. 5), there is a clear trend showing that the more highly graphitized the fibers are, the lower is their thermal stability. This is shown clearly also in figure 4, which plots the resistance ratio after 24 hr exposure as a function of exposure temperature.

Comparing figure 3 with figure 5 reveals the effect of replacing Br_2 with ICl. At temperatures below 200 °C P-120, P-100, P-75, and P-55 fibers intercalated with ICl lose conductivity at a rate that appears to be independent of fiber type. This may be the result of out-gassing of ICl to the final residual concentration, a process which happens so rapidly in the brominated fiber that it is completed before the stability tests were initiated. Only above 200 °C is differentiation observed among the fiber types. When this does occur, again we find that the less graphitic the fiber, the better the thermal stability. This is emphasized in figure 6, which plots the resistance ratio after 24 hr of exposure as a function of temperature (similar to fig. 4). The poor stability for ICl below 200 °C may be an indication of fundamental differences between the reaction of Br_2 and ICl with pitch-based graphite fibers. As judged by the high temperature data ICl appears to have lower thermal stability than Br_2. This may be somewhat surprising because ICl requires higher temperatures before a reaction occurs. The conventional wisdom has been that intercalates which require higher temperatures to react will also be stable at higher temperatures. Here are two very closely related intercalates that refute that assertion.

The thermal stability of the resistance of $CuCl_2$ intercalated P-55, P-75, P-100, and P-120 fibers is shown in figures 7 and 8. One first notes that the thermal stability is much lower than for either of the halogen GIC's. Even the most stable compound, $CuCl_2$ in P-55, was so reactive that meaningful data could only be obtained up to about 250 °C. Thermogravimetric analysis (TGA) on graphite powders intercalated with $CuCl_2$ reveals weight loses which occur when the temperature exceeds about 250 °C. These two observations are doubtlessly linked and probably signal the onset of deintercalation.

The thermal stability of the resistance of $NiCl_2$ intercalated P-100 and P-120 fibers is summarized in figures 9 and 10. The thermal stability is considerably higher than that of the $CuCl_2$ analog, with data up to 350 °C being generally reproducible. TGA on $NiCl_2$ intercalated powders reveal weight losses which begin at 350 °C. Thus, deintercalation of $NiCl_2$ appears to be similar to $CuCl_2$, but occurs at a higher temperature. The stability is comparable to that of the ICl analog, although somewhat lower than Br_2. The $NiCl_2$ compounds were also similar to the ICl compounds in that even at very low temperatures there was some degradation of the resistance.

Applications Implications

The results of this study have implications for the viability of these fibers as practical engineering materials. Table II shows the resistivity values of each of the fiber types after 30 days at ambient conditions. It reveals that pitch-based graphite fibers intercalated with Br_2, ICl, or $NiCl_2$, and P-55 and P-75 fibers intercalated with $CuCl_2$, have shelf lives of at least this duration, provided the humidity is kept low. If the humidity is allowed to remain high for even short periods of time, the resistivity of $CuCl_2$ and $NiCl_2$ intercalated fibers increases dramatically, as illustrated by table III, which shows the resistivity after only five days at 100 percent humidity at 60 °C.

Caution must be exercized when trying to relate these results to possible applications. What has been stressed throughout this paper is environmental stability of the intercalated fibers themselves. In most applications these

fibers will be embedded in a polymer matrix, and that could effect the stability characteristics. Although water travels rather freely through most matrix materials, there may be synergistic effects which could affect the relative rates of degradation due to water in the environment. The partition coefficient for water between the resin and the fibers could either effectively seal the fibers from the environment, or continually feed water to the fibers even when the ambient humidity is low.

Additionally, the fibers would be exposed to various organic solvents during processing, and these effects have not been greatly investigated. Brominated P-100 fibers are known to be stable to a wide variety of solvents for at least several days (ref. 11). $CuCl_2$ intercalated powders are stable in non-polar solvents, but degrade quickly in polar solvents, most notably methanol (ref. 12).

Several criteria must be examined before choosing a fiber-intercalate system for a particular application. Mechanical properties, resistivity, stability, and cost must all come into play. The only commercially available graphite fibers which have proven feasible at this time for intercalation are pitch-based fibers, such as those reported here, and some very graphitic PAN-based fibers (ref. 13). The resistivity after 24 hr heated in air as a function of temperature for the fiber types investigated in this study is a reminder that what appear to be large percentage increases may indeed be small absolute increases (fig. 11).

CONCLUSIONS

It has been shown here that the decreases in the resistivity of pitch-based graphite fibers brought about by intercalation are not as dependant upon the extent of graphitization as might be supposed. Within each intercalate the ratios of pristine to intercalated resistance are within 10 percent for P-120, P-100, and P-75 fibers. There seems to be a large difference between the higher modulus fibers and the intercalation compounds with P-55, the latter showing less resistance drop upon reaction. The order of conductivity improvement by intercalation for all of the fiber types is ICl (most improvement) > Br_2 > $CuCl_2$ > $NiCl_2$ (least improvement). The order of conductivity improvement of the fibers by all of the intercalates is P-120 = P-100 = P-75 > P-55.

The only intercalate which exhibits absolute ambient stability with all of the fiber hosts is Br_2. In addition, ICl in P-55 and P-75 fibers appear to have absolute ambient stability. ICl intercalated P-100 and P-120 fibers have very good ambient stability, degrading only about 1 percent after several months. The resistance of $NiCl_2$ intercalated P-100 and P-120 fibers degrades by at least 5 percent over several weeks. The P-55 and P-75 fibers which were intercalated with $CuCl_2$ also degrade by a few percent over several weeks. The largest resistance changes in ambient conditions were observed in P-100 and P-120 fibers intercalated with $CuCl_2$. These were of the order of a factor of 2 within a few days. It is believed that the principal cause of instabilities at ambient conditions is the uptake of water from the air. This is supported by the results of the vacuum experiments, which indicate that the GIC's are inherently stable at room temperature, and by the results of the humidity experiments, which were exaggerations the of the ambient conditions test.

The humidity stability results again show that Br_2 is stable in all of the fiber hosts. ICl exhibits degradation of only a few percent over several months. P-55 and P-75 fibers intercalated with $CuCl_2$ degrade by about 70 percent over several days. P-100 and P-120 fibers intercalated with either $CuCl_2$ or $NiCl_2$ had their resistances increase by about a factor of 3 over a few days time. In all fibers the order of humidity stability of intercalates is Br_2 (most stable) > ICl >> $CuCl_2$ = $NiCl_2$. In all intercalates the order of humidity stability of fibers is P-55 (most stable) > P-75 >> P-100 = P-120 (least stable).

All of the intercalate-fiber combinations tested were stable to a vacuum of 10^{-4} Pa (10^{-6} torr) for at least several days.

The thermal stability varied widely over the ranges of intercalates and fiber hosts. This data is summarized in table IV, which shows the resistance ratio for each fiber, intercalate, and test temperature after 24 hr. The order of thermal stability in air for the intercalates in all fibers is Br_2 (most stable) > ICl > $NiCl_2$ > $CuCl_2$ (least stable). The order of thermal stability for the fiber types is P-55 (most stable) > P-75 > P-100 > P-120 (least stable).

The overall stability trends are obvious from this study. Bromine remains the intercalate of choice if stability is the criteria. It outperformed ICl, $CuCl_2$, $NiCl_2$, and, at least in P-100 fibers, $FeCl_3$ (ref. 4). In fact the only serious challenge comes from ICl, which has the advantages of slightly better improvement in the resistance (by about 10 percent) and the ability to intercalate P-55 fiber. The latter has important implications because of the economic advantage of using P-55 over the other fiber types. The transition metal chlorides appear to be seriously susceptable to water vapor and high temperature. However, it should again be cautioned that matrix effects when these fibers are made into composites may be considerable.

In a previous paper the concept of "threshold graphitization" was put forward with respect to the ability of a fiber to react with an intercalate (ref. 5). This idea can be expanded to include the humidity stability trends. It is obvious, when the humidity stability is examined, that intercalation compounds of P-55 and P-75 are much more stable than those of P-100 and P-120. Perhaps the idea of a threshold graphitization, above which humidity stability rapidly decreases, should be considered. If the humidity stability is controlled by the diffusion of water into the graphite lattice then it should be completely analogous to an intercalation threshold of graphitization. This would explain why all of the large decreases in humidity stability occur when the graphitization is increased from P-75 to P-100, no matter which intercalate is used. That the threshold for water occurs at a different graphitization than for bromine simply reflects the differing diffusion coefficients of the two species.

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TABLE I. - INITIAL RESISTIVITIES OF INTERCALATED GRAPHITE FIBERS IN μΩ-cm

Intercalate	P-55	P-75	P-100	P-120
Pristine	900	500	250	220
Br_2	868	120	52	50
ICl	300	100	46	44
$CuCl_2$	330	110	80	90
$NiCl_2$	---	430	80	60

TABLE II. - RESISTIVITIES, IN μΩ-cm, OF INTERCALATED GRAPHITE FIBERS STORED IN AMBIENT LABORATORY AIR FOR 30 DAYS

Intercalate	P-55	P-75	P-100	P-120
Pristine	900	500	250	220
Br_2	868	120	52	50
ICl	303	100	47	45
$CuCl_2$	328	109	173	159
$NiCl_2$	---	---	82	61

Table III. - RESISTIVITIES, IN μΩ-cm, OF INTERCALATED GRAPHITE FIBERS STORED AT HIGH HUMIDITY FOR 5 DAYS

Intercalate	P-55	P-75	P-100	P-120
Pristine	900	500	250	220
Br_2	868	120	52	50
ICl	308	102	46	44
$CuCl_2$	534	196	237	270
$NiCl_2$	---	---	299	192

Table IV. - RESISTANCE RATIO (R/R_o) AFTER 24 HR AT THE TEST TEMPERATURE IN AIR

Fiber Inter	100 °C	150 °C	200 °C	250 °C	300 °C	350 °C	400 °C
P-55 $CuCl_2$	1.02	1.03	1.06	1.60	2.26	----	----
P-55 ICl	1.02	1.04	1.05	1.05	1.12	----	----
P-75 $CuCl_2$	1.01	1.11	1.32	2.38	2.88	----	----
P-75 Br_2	1.00	1.00	1.00	1.00	1.03	1.11	1.26
P-75 ICl	1.02	1.04	1.07	1.08	1.15	1.28	1.53
P-100 $CuCl_2$	1.04	1.08	1.37	4.43	6.60	----	----
P-100 $NiCl_2$	1.04	1.05	1.10	1.13	1.19	1.38	7.08
P-100 Br_2	1.00	1.00	1.00	1.01	1.13	1.11	1.38
P-100 ICl	1.00	1.02	1.07	1.11	1.20	1.30	1.39
P-120 $CuCl_2$	1.02	1.03	1.05	1.61	3.32	----	----
P-120 $NiCl_2$	1.04	1.06	1.15	1.15	1.24	1.34	4.69
P-120 Br_2	1.00	1.00	1.00	1.04	1.10	1.20	1.66
P-120 ICl	1.00	1.04	1.13	1.19	1.39	1.46	1.58

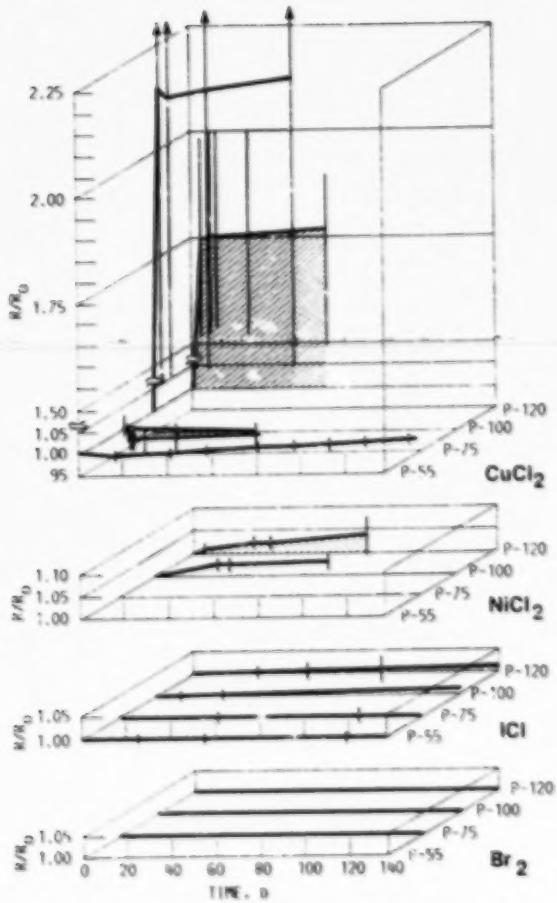

FIGURE 1. - RESISTANCE RATIO (RESISTANCE, R/INITIAL RESISTANCE, R_0) AS A FUNCTION OF TIME EXPOSED TO AMBIENT AIR FOR P-120, P-100, P-75, AND P-55 GRAPHITE FIBERS INTERCALATED WITH BROMINE, IODINE MONOCHLORIDE, COPPER (II) CHLORIDE, AND NICKEL (II) CHLORIDE. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

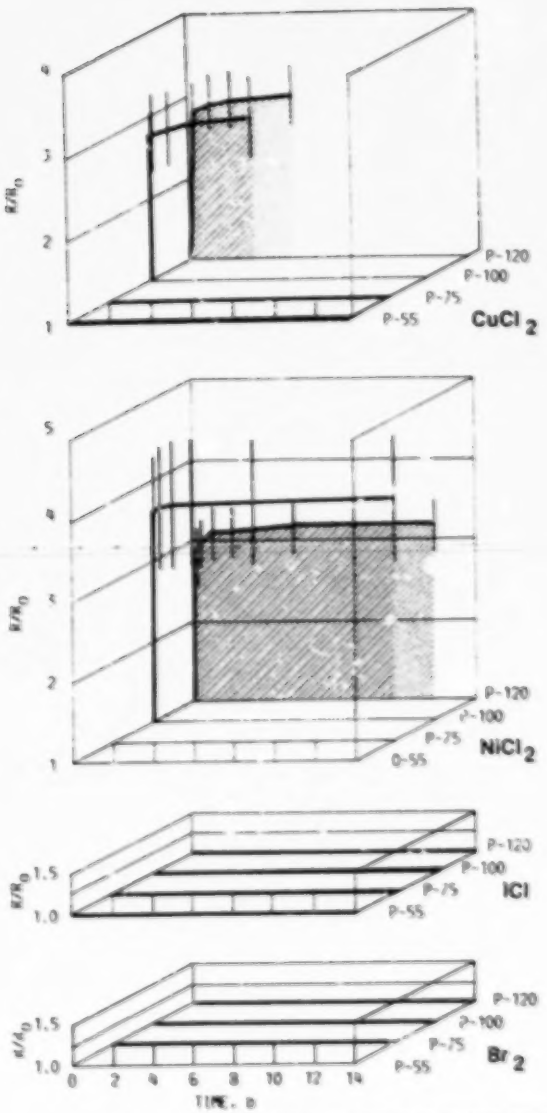

FIGURE 2. - RESISTANCE RATIO AS A FUNCTION OF TIME EXPOSED TO 100% HUMIDITY AT 60 °C FOR P-120, P-100, P-75, AND P-55 GRAPHITE FIBERS INTERCALATED WITH BROMINE, IODINE MONOCHLORIDE, COPPER (II) CHLORIDE, AND NICKEL (II) CHLORIDE. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

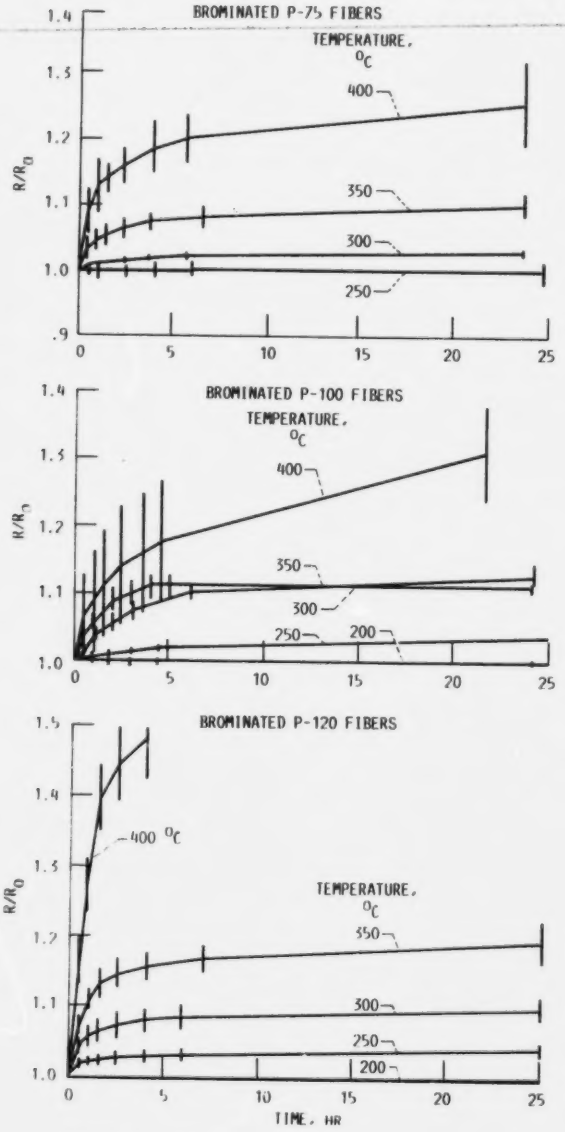

FIGURE 3. - RESISTANCE RATIO AS A FUNCTION OF TIME EXPOSED TO 200 TO 400 °C AIR FOR P-120, P-100, AND P-75 GRAPHITE FIBERS INTERCALATED WITH BROMINE. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

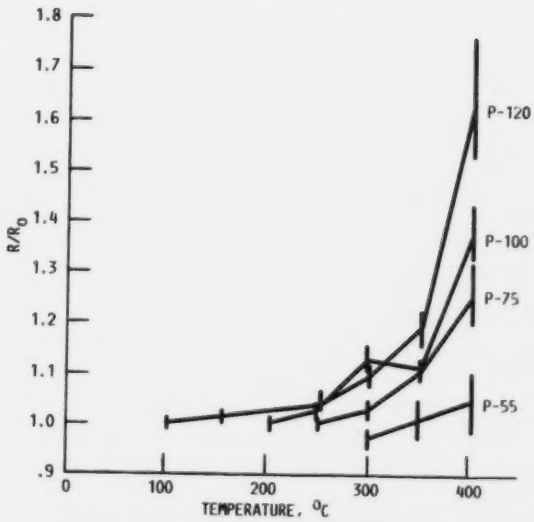

FIGURE 4. - RESISTANCE RATIO AS A FUNCTION OF TEMPERATURE FOR BROMINATED P-75, P-100, AND P-120 GRAPHITE FIBERS AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

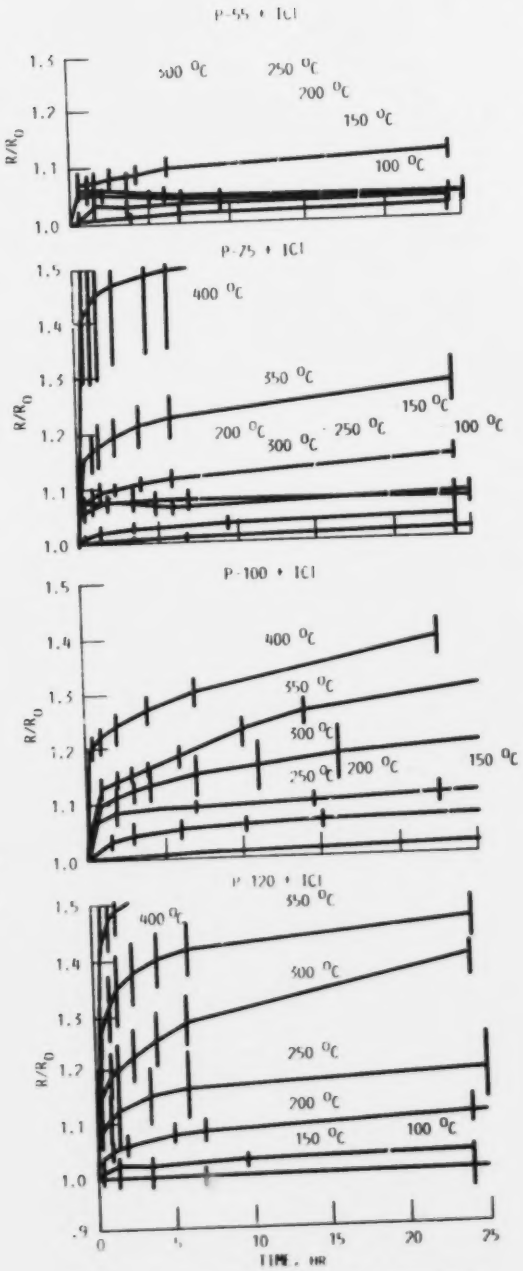

FIGURE 5. - RESISTANCE RATIO AS A FUNCTION OF TIME EXPOSED TO 100 TO 400 °C AIR, FOR P-120, P-100, P-75, AND P-55 GRAPHITE FIBERS INTERCALATED WITH IODINE MONOCHLORIDE. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

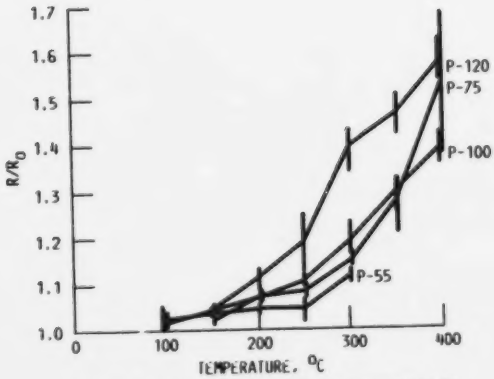

FIGURE 6. - RESISTANCE RATIO AS A FUNCTION OF TEMPERATURE FOR P-55, P-75, P-100 AND P-120 GRAPHITE FIBERS INTERCALATED WITH IODINE MONOCHLORIDE AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

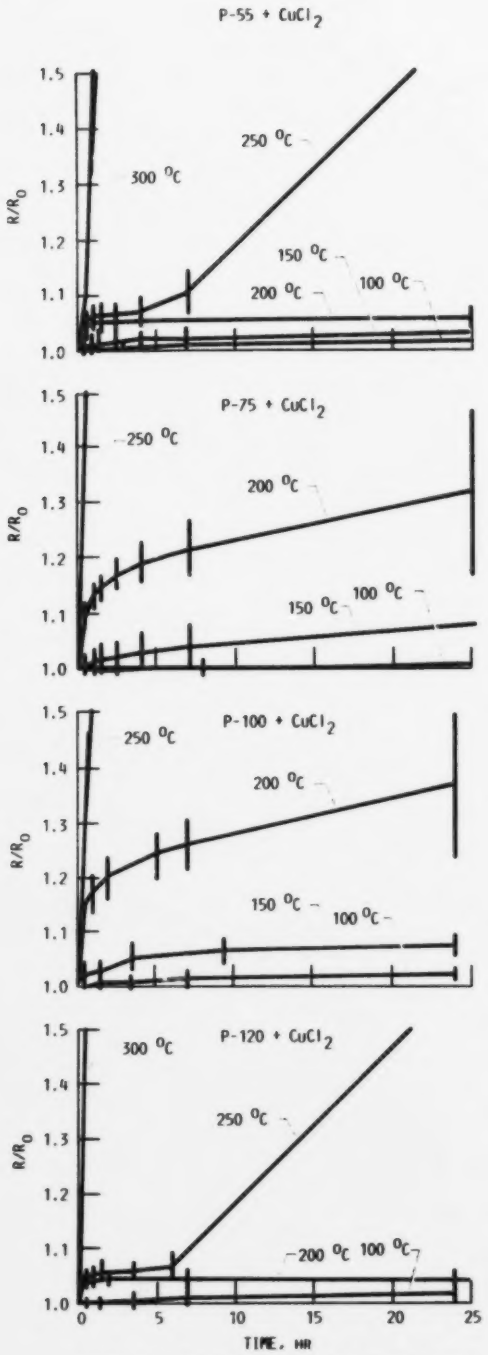

FIGURE 7. - RESISTANCE RATIO AS A FUNCTION OF TIME EXPOSED TO 100 TO 300 °C AIR FOR P-120, P-100, P-75, AND P-55 GRAPHITE FIBERS INTERCALATED WITH COPPER (II) CHLORIDE. VERTICAL LINES INDICATE THE SAMPLE STANDARD DEVIATION.

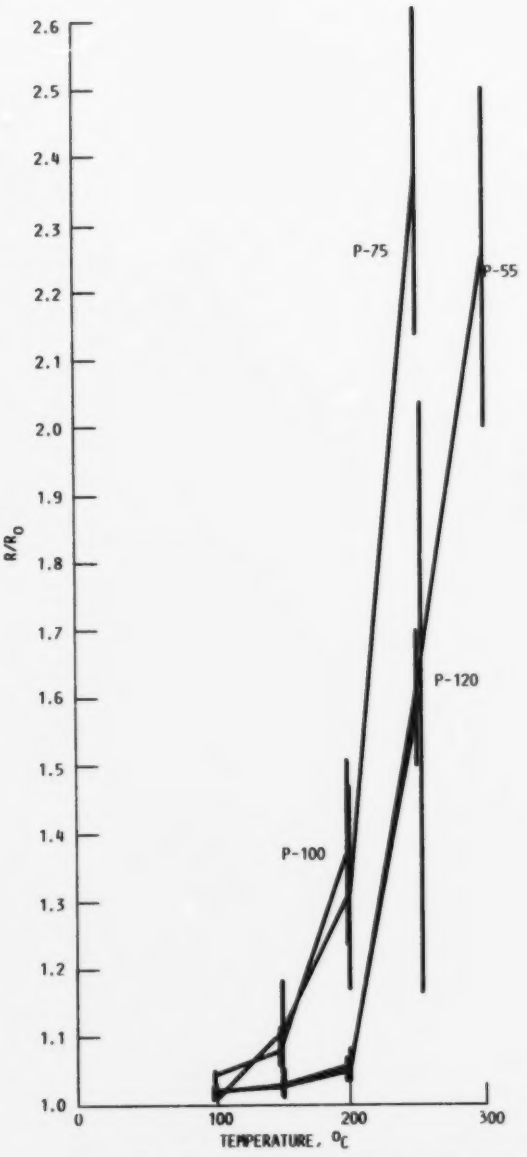

FIGURE 8. - RESISTANCE RATIO AS A FUNCTION OF TEMPERATURE FOR P-55, P-75, P-100, AND P-120 GRAPHITE FIBERS INTERCALATED WITH COPPER (II) CHLORIDE AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

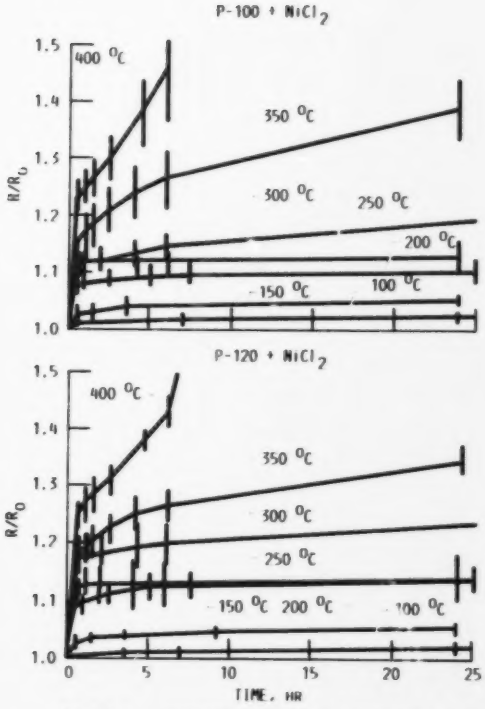

FIGURE 9. - RESISTANCE RATIO AS A FUNCTION OF TIME EXPOSED TO 100 TO 400 °C AIR FOR P-120 AND P-100 GRAPHITE FIBERS INTERCALATED WITH NICKEL (II) CHLORIDE. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

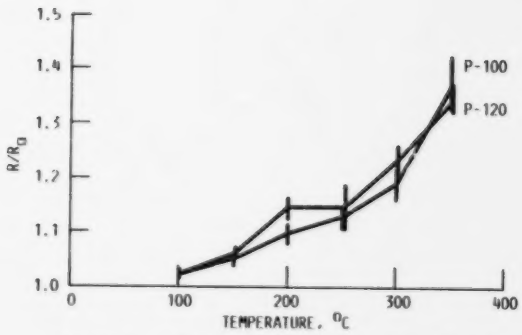

FIGURE 10. - RESISTANCE RATIO AS A FUNCTION OF TEMPERATURE FOR P-100 AND P-120 GRAPHITE FIBERS INTERCALATED WITH NICKEL (II) CHLORIDE AFTER 24 HOURS EXPOSURE TO TEMPERATURE IN AIR. VERTICAL LINES INDICATE SAMPLE STANDARD DEVIATION.

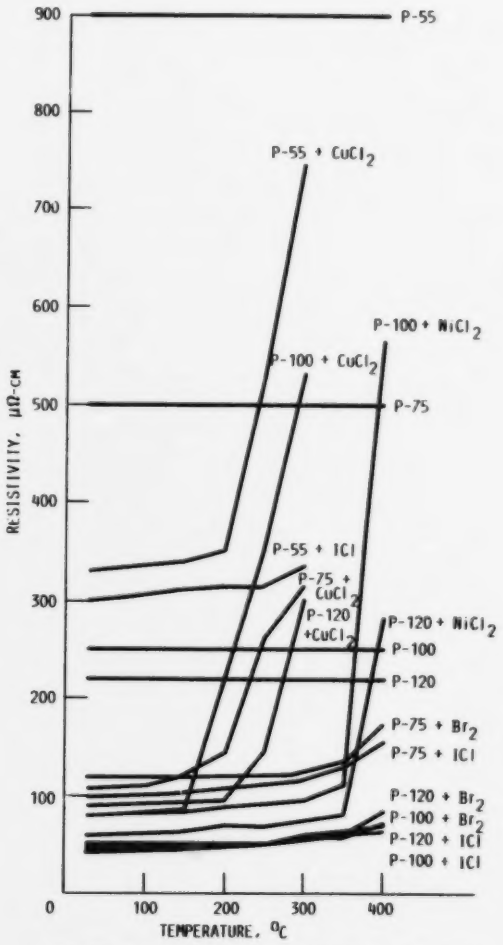

FIGURE 11. - RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR FIBER INTERCALATION COMPOUNDS INVESTIGATED IN THIS STUDY.

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15. Supplementary Notes

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16. Abstract

Four different grades of pitch-based graphite fibers (Amoco P-55, P-75, P-100, and P-120) were intercalated with each of four different intercalates: bromine (Br_2), iodine monochloride (ICl), copper (II) chloride ($CuCl_2$), and nickel (II) chloride ($NiCl_2$). The P-55 fibers did not react with Br_2 or $NiCl_2$, and the P-75 did not react with $NiCl_2$. The stability of the electrical resistance of the intercalated fibers was monitored over long periods of time in ambient, high humidity (100 percent at 60 °C), vacuum (10^{-6} torr), and high temperature (up to 400 °C) conditions. It was found that fibers with lower graphitization form graphite intercalation compounds (GIC's) which are more stable than those with higher graphitization (i.e., P-55 (most stable) > P-75 > P-100 > P-120 (least stable)). Br_2 formed the most stable GiC's followed in order of decreasing stability by ICl, $CuCl_2$, and $NiCl_2$. While Br_2 GIC's had the best stability, ICl had the advantages of forming GIC's with slightly greater reduction in resistance (by about 10 percent) than Br_2, and the ability to intercalate P-55 fiber. The transition metal chlorides appear to be seriously susceptible to water vapor and high temperature. However, it should be cautioned that matrix effects when these fibers are made into composites may cause the composite stabilities to differ from these single fiber results.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Graphic intercalation compounds; Graphite fibers; Bromine; Iodine monochloride; Copper (II) chloride; Nickel (II) chloride; Stability	Unclassified - unlimited STAR Category 27

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